



# Innovative carbon-free low content Pt catalyst supported on Mo-doped titanium suboxide ( $\text{Ti}_3\text{O}_5$ -Mo) for stable and durable oxygen reduction reaction

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## ABSTRACT

Recently the use of titanium oxide and titanium suboxides (Magnéli phases) has been extensively investigated as an alternative catalyst support to carbon-based materials for the oxygen reduction reaction in low-temperature fuel cells. In this study, a 15 wt.% Pt-based catalyst was developed on a unique, stable mix of titanium suboxides, with a prevailing of the  $\text{Ti}_3\text{O}_5$  phase, doped with Mo, as a  $\text{Ti}_3\text{O}_5$ -Mo carbon-free support and compared to a commercial 20 wt.% Pt/C (E-TEK). The Pt/ $\text{Ti}_3\text{O}_5$ -Mo catalyst exhibits excellent electroactivity and stability toward the ORR, reaching a performance of  $73.3 \text{ mA mg}^{-1}$ , slightly more than the double of the commercial Pt/C, with a current density of  $1.1 \text{ mA cm}^{-2}$  at 0.9 V vs RHE, and an half-wave potential of 0.86 V vs RHE. A deep accelerated potential cycling between 0 and 1.2 V vs RHE up to 5000 cycles demonstrated the remarkable stability of the Pt/ $\text{Ti}_3\text{O}_5$ -Mo catalyst, whose electrochemical surface area loss was accounted for only 11%, compared to the more than 81% loss of the commercial Pt/C reference

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## 1. Introduction

Platinum (Pt), which is a highly efficient catalyst, is widely applied in proton exchange membrane fuel cells (PEMFCs) as cathodic side for the oxygen reduction reaction (ORR:  $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ ). In the application of Pt catalysts, the supporting material is one of the most important factors when looking to enhance the electroactivity and stability of the catalyst. Carbon materials are extensively employed to support Pt catalysts in PEMFCs due to their excellent conductivity and high specific surface area. However, one of the main drawbacks of carbon supported catalysts is located at the cathode, which the electrode potential is relatively high in an acidic environment and carbon materials suffer corrosion under these conditions ( $\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CO}_2 + 4\text{H}^+ + 4\text{e}^-$ , 0.207 V vs NHE at 25 °C). As a consequence, dissolution and agglomeration of Pt particles occur resulting in a decrease of electroactivity of the catalyst [1–4]. The Pt dissolution, which is an anodic reaction, causes a mixed potential at the cathode and subsequently the negative shifting of the ORR reversible potential. As a result, a

huge decrease of the long-term stability of the catalyst performance occurs [1].

Among the candidates available for metal oxides supports, considerable attention has been paid to titanium suboxides ( $\text{Ti}_x\text{O}_{2x-1}$ , even known as Magnéli phases of titanium oxide) as a non-carbon material with high electronic conductivity, stability, and durability in acidic media. Substoichiometric Magnéli phases obtained from thermally treated  $\text{TiO}_2$  in a reducing environment have electron conductivity similar to graphite thanks to oxygen vacancies in the crystalline lattice [5]. Moreover, chemically inert titanium suboxides materials are chosen because of economic reasons. These qualities make titanium suboxides an appropriate support for Pt-based catalyst utilization in PEMFC and DMFC [6–9], in particular for hydrogen fuel cell vehicles [5]. According to Walsh and Wills [10], the electrical conductivity of  $\text{Ti}_x\text{O}_{2x-1}$  depends on the suboxide 'x' value, but it is of the same order of magnitude as carbon. The electrical conductivity is greatest for  $x=3$  to 5, and it decreases at higher 'x' values. According to the literature, employing titanium suboxides instead of carbon as a support has the undoubted advantages of reducing the OH adsorption on Pt surface by lateral repulsion from the OH or O on the suboxide's support surface, and enhanced splitting of the O–O bond which is caused by the presence of oxygen vacancy sites on titanium suboxides support and preventing the dissolution of Pt from the surface of the

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support [11–16]. Moreover, the presence of  $\text{Ti}^{3+}$  defects and/or oxygen vacancies in titanium suboxides can act as a charge electron recombination centers, with a beneficial role in catalysis and photocatalysis, by reducing the electron-hole pair recombination rate [17,18], and favoring the  $d-d$  transition. Typically, titanium oxides containing  $\text{Ti}^{3+}$  show black or dark blue color because of the  $d-d$  transition on  $\text{Ti}^{3+}$  [19,20].

Among all possible titanium suboxides, trititanium pentoxide ( $\text{Ti}_3\text{O}_5$ ) has been extensively investigated, and it exists in a variety of structural polymorphs, as a potential material for oxygen sensor and for photocatalytic properties [21–23]. Trititanium pentoxide is a metal-like compound with high conductive properties (conductivity higher than  $600 \text{ S cm}^{-1}$ ) [10,24].

Since  $\text{TiO}_2$  is a very stable compound, the formation of titanium suboxides in reducing environment requires long exposure at very high temperatures ( $>1200^\circ\text{C}$ ). The presence of a metal, such as Mo, Co, Ni, Cu, [1,5,21] favors the evolution of  $\text{TiO}_2$  into Magnéli phases at much lower temperatures. Moreover, according to the literature [25–27],  $\text{Ti}_x\text{O}_{2x-1}\text{-M}$  (with  $\text{M}=\text{Co}, \text{Ni}, \text{Cu}, \text{Mo}, \text{Ru}, \text{Ir}$ ) as support plays a co-catalytic function together with Pt nanoparticles toward ORR. These supports not only solve the above-mentioned carbon-corrosion issues but also enhance the catalytic activity for ORR, due to strong metal-support interaction between the metal oxide and the Pt catalyst.

$\text{Pt/Ti}_3\text{O}_5\text{-Mo}$  exhibits excellent properties as a catalyst due to the structural and electronic properties of  $\text{Ti}_3\text{O}_5\text{-Mo}$  [27–29]. In particular,  $\text{Ti}_3\text{O}_5\text{-Mo}$  has a high resistance to electrochemical corrosion which enhances the durability of the Pt catalyst. The positive effect due to the trititanium pentoxide is explained by considering the changes in Pt- $d$  electronic properties and the geometric effect that produces the contraction of Pt–Pt bonding distance [30,31], leading to a favorable condition for electrochemical reactions. The activity enhancement of binary  $\text{Pt/Ti}_3\text{O}_5\text{-Mo}$  catalysts is attributed to the electronic donation of  $\text{Ti}_3\text{O}_5\text{-Mo}$  to Pt surface, which modifies the electronic structure of Pt surface atoms resulting in a weakened interaction between Pt and intermediates, freeing more active sites for  $\text{O}_2$  adsorption [32]. This results in strong physical and chemical interaction with adsorbed gas species [33–35]. Finally, in our recent studies, we found out that the presence of  $\text{Ti}_3\text{O}_5$  suboxide in a series of Pt/C-TiOx-C catalysts positively improves the performance toward the ORR, enhancing the stability under potential cycling [36].

In this study, a comparative evaluation of the structure, composition and electrochemical performance of the  $\text{Pt/Ti}_3\text{O}_5\text{-Mo}$  catalysts is discussed. A Pt layer was homogeneously deposited over the surface of the  $\text{Ti}_3\text{O}_5\text{-Mo}$  support. The resulting  $\text{Pt/Ti}_3\text{O}_5\text{-Mo}$  catalyst with intrinsic electrocatalytic activity and excellent stability in acidic media was applied toward the ORR. These efforts indicate that both Pt morphology and support structure can significantly enhance the catalytic activity and stability. The  $\text{Pt/Ti}_3\text{O}_5\text{-Mo}$  catalyst was characterized by X-ray diffraction (XRD), inductively coupled plasma atomic mass spectroscopy (ICP-MS), X-ray photoemission spectroscopy (XPS), transmission electron microscopy (TEM), field-emission scanning electron microscopy (FESEM), UV-vis measurements, and electrochemical long-term activity testing, including cyclic voltammetry (CV), linear sweep voltammetry (LSV), and accelerated potential cycling test (APCT).

## 2. Experimental part

### 2.1. Chemicals

Titanium (IV) oxide, anatase ( $\text{TiO}_2$ ) 99.8 wt.%, chloroplatinic acid hexahydrate ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ )  $\geq 37.50\%$  Pt basis, sodium borohydride ( $\text{NaBH}_4$ ) 98 wt.%, potassium hydroxide (KOH)

85 wt.%, ammonium hydroxide ( $\text{NH}_4\text{OH}$ ) 28.0%  $\text{NH}_3$  basis, polyvinylpyrrolidone (PVP40:  $(\text{C}_6\text{H}_9\text{NO})_n$  average molar weight 40,000), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Pluronic® 123, average molar weight 5800), sulfuric acid ( $\text{H}_2\text{SO}_4$ ) 95–98 wt.%, perchloric acid ( $\text{HClO}_4$ ) 70 wt.%, Nafion® perfluorinated resin solution 5 wt.%, acetone ( $\text{CH}_3\text{COCH}_3$ ) 99.5 wt.%, 2-propanol ( $\text{C}_3\text{H}_8\text{O}$ ) 99.5 wt.%, and ammonium molybdate ( $\text{H}_{24}\text{Mo}_7\text{N}_6\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ) were purchased from Sigma-Aldrich. A commercial platinum catalyst 20 wt.% on carbon black Vulcan XC-72R purchased from E-TEK was used for comparison tests. Nitrogen and oxygen gases were supplied in cylinders by SIAD with 99.999% purity. All aqueous solutions were prepared using ultrapure water obtained from a Millipore Milli-Q system with resistivity  $>18 \text{ m}\Omega \text{ cm}$ .

### 2.2. Synthesis of titanium suboxide ( $\text{Ti}_3\text{O}_5\text{-Mo}$ )

The titanium suboxide  $\text{Ti}_3\text{O}_5$  was prepared by doping commercial  $\text{TiO}_2$  anatase with Mo ions.  $\text{TiO}_2$  was dispersed in a solution of (70:30 vol.%) ultrapure water and ethanol respectively, followed by the addition of 2 wt.% Pluronic P123 surfactant. The obtained solution was stirred for 5 h at ambient temperature. Then 10 wt.% of Mo ( $\text{H}_{24}\text{Mo}_7\text{N}_6\text{O}_{24} \cdot 4\text{H}_2\text{O}$ ) was added to the solution. The pH of the solution was held constant at  $\text{pH}=9$  by adding  $\text{NH}_4\text{OH}$ . The mixed solution was continuously stirred at room temperature for other 5 h, evaporated at  $120^\circ\text{C}$ , and finally dried at  $80^\circ\text{C}$  for 12 h. The obtained powder was annealed at  $850^\circ\text{C}$  (heating rate of  $10^\circ\text{C min}^{-1}$ ) for 8 h under a reducing atmosphere ( $\text{H}_2:\text{N}_2$  10:90 vol.%).

### 2.3. Synthesis of $\text{Pt/Ti}_3\text{O}_5\text{-Mo}$

100 mg of  $\text{Ti}_3\text{O}_5\text{-Mo}$  support was dispersed in a solution of ultrapure deionized water and ethanol (30:10 mL) followed by adding 1 wt.% PVP surfactant. The solution was brought to  $\text{pH}$  9–10 by adding  $\text{NH}_4\text{OH}$  and left stirring for 1 h. Then, 39.82 mg of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  was dissolved in 10 mL of ultrapure deionized water and slowly reduced by adding 1 wt.%  $\text{NaBH}_4$  at room temperature. This was then added to the support solution and left stirring for 5 h at an ambient temperature. The obtained solution was sonicated for 1 h and later left to stir for 5 h to allow for Pt adsorption. The resulting catalyst obtained after drying was heat-treated at  $450^\circ\text{C}$  (heating rate of  $5^\circ\text{C min}^{-1}$ ) for 5 h under a reducing atmosphere ( $\text{H}_2:\text{N}_2$  10:90 vol.%).

### 2.4. Chemical-physical characterization

The platinum-to-support weight percentage in the synthesized  $\text{Pt/Ti}_3\text{O}_5\text{-Mo}$  catalyst was determined by ICP-MS with a ThermoFisher Scientific ICAP-Q instrument. Prior to analysis, the samples were digested in hot concentrated  $\text{HCl}/\text{HNO}_3$  3:1 mixture with some droplets of  $\text{H}_2\text{SO}_4$ .

The XRD patterns were recorded on a Panalytical X'Pert PRO diffractometer with a PIXcel detector, using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.15418 \text{ nm}$ ), under the operating conditions of  $2\theta = 20 - 90^\circ$  and  $2\theta$  step size = 0.03, in order to examine the different polymorphs. The markers were located using the Philips X'Pert HighScore Software (ICDD database). The morphology of the support and the catalysts, and the characterization of the metals were observed by FESEM (JEOL-JSM-6700F instrument coupled with an energy dispersive X-ray spectroscopy (EDX) detector by OXFORD INCA). For the support, the STEM modality was employed to better enlighten the presence of Mo. The support was deposited on a copper grid with a graphitic carbon layer. TEM was carried out using a JEOL-2000 FXII microscope equipped with a LaB6 gun. 0.5 mg of samples was dispersed in 5 mL isopropyl alcohol and sonicated for

3 h, later, 5  $\mu\text{L}$  of the solution was dropped on the surface of the copper grid and dried under  $\text{N}_2$  atmosphere.

Diffuse Reflectance (DR) UV–vis spectra of outgassed commercial  $\text{TiO}_2$  and synthesized  $\text{Ti}_3\text{O}_5$ -Mo were performed (Agilent Cary 5000 UV–vis-NIR spectrometer) to measure the optical absorption and band gap values by applying the Tauc equation.

XPS analysis was performed to determine the elemental surface composition of the catalysts. The analysis was carried out using a Physical Electronics PHI 5000 Versa Probe electron spectrometer system with monochromated Al K $\alpha$  X-ray source (1486.60 eV) running at 15 kV and 1 mA anode current. The survey spectra were collected from 0 to 1200 eV. The narrow Pt 4f spectra were collected from 60 to 90 eV, the narrow Mo 3d spectra from 220 to 248 eV, and the narrow Ti 2p spectra from 444 to 480 eV. All of the spectra were calibrated against a value of the C 1s binding energy of 284.5 eV. Multipack 9.0 software was used for obtaining semi-quantitative atomic percentage compositions, using Gauss-Lorentz equations with the Shirley-type background. A 70%/30% Gaussian/Lorentzian line shape was used to evaluate peaks position and areas of the high-resolution spectra.

### 2.5. Electrochemical characterization

The catalysts were characterized using CV, LSV, and CO stripping voltammetry measurements. All the electrochemical characterizations were carried out in a three-compartment electrochemical cell using a multi-potentiostat (Bio-Logic SP150), and a rotating disk electrode mounted on a rotating ring disk electrode apparatus (RRDE-3A ALS Model 2323). As the electrolyte, both a 0.5 M  $\text{H}_2\text{SO}_4$  and a 0.1 M  $\text{HClO}_4$  aqueous solutions were used and saturated with either  $\text{N}_2$  or  $\text{O}_2$  pure gas by direct bubbling into the solution. For RDE measurements, the cell was equipped with a glassy carbon (GC) disk working electrode (0.07  $\text{cm}^2$  geometric area), a carbon graphite as a counter electrode and a reference hydrogen electrode (RHE).

The catalyst ink was prepared dissolving 7.0 mg of the catalyst in 0.6 mL of  $\text{H}_2\text{O}$ , 1 mL of isopropyl alcohol IPA and using an ionomer-to-catalyst (ITC) mass ratio (mg of Nafion<sup>®</sup> over mg of catalyst) equal to 0.1 and calculated Pt quantity loading of 15  $\mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ , corresponding to 3  $\mu\text{L}$  of the sonicated ink. This mixture was sonicated for 30 min and then stirred for 2 h. Then, the catalyst ink was pipetted onto a glassy carbon electrode so that the catalyst film contained 76.9 nmol of Pt. The working electrode was polished with 1 and 0.06 mm alumina powders to mirror-like finish its surface and sonicated to remove alumina particles before each experiment.

CV was recorded in  $\text{N}_2$ -purged 0.5 M  $\text{H}_2\text{SO}_4$  and 0.1 M  $\text{HClO}_4$  to obtain the background capacitive current and the electrochemical surface area (ECSA) of the Pt catalyst which was conducted at room temperature and a scan rate of 10  $\text{mV s}^{-1}$ . To clean the surface of Pt catalyst, each electrode was cycled 30 times in  $\text{N}_2$ -purged 0.5 M  $\text{H}_2\text{SO}_4$ , sweeping in the potential range of 0.0–1.5 V vs RHE at a scan rate of 100  $\text{mV s}^{-1}$ . The ECSA ( $\text{m}^2 \text{g}^{-1}$ ) of the catalysts was determined from the Pt-hydrogen desorption region between 0.0 V and 0.4 V vs RHE, by integrating the total charge, normalizing with scan rate, Pt loading, and assuming a surface charge density of 210  $\mu\text{C cm}^{-2}$  for a monolayer adsorption of hydrogen on Pt surface [4,43].

CO-stripping voltammetry was performed in 0.5 M  $\text{H}_2\text{SO}_4$  and 0.1 M  $\text{HClO}_4$  at a scan rate of 20  $\text{mV s}^{-1}$ . Prior to the analysis, a flow rate of CO was pre-adsorbed for 15 min while the working electrode was maintained at the constant potential of 0.06 V vs RHE. Afterward, a flow rate of pure  $\text{N}_2$  was introduced for 20 min to remove the CO dissolved in the solution before stripping the CO. LSV was conducted in 0.5 M  $\text{H}_2\text{SO}_4$  and 0.1 M  $\text{HClO}_4$  solution by bubbling  $\text{O}_2$  gas at room temperature at a scan rate of 5  $\text{mV s}^{-1}$  and rotating disk speed of 900 rpm.  $\text{O}_2$  was bubbled directly into the cell

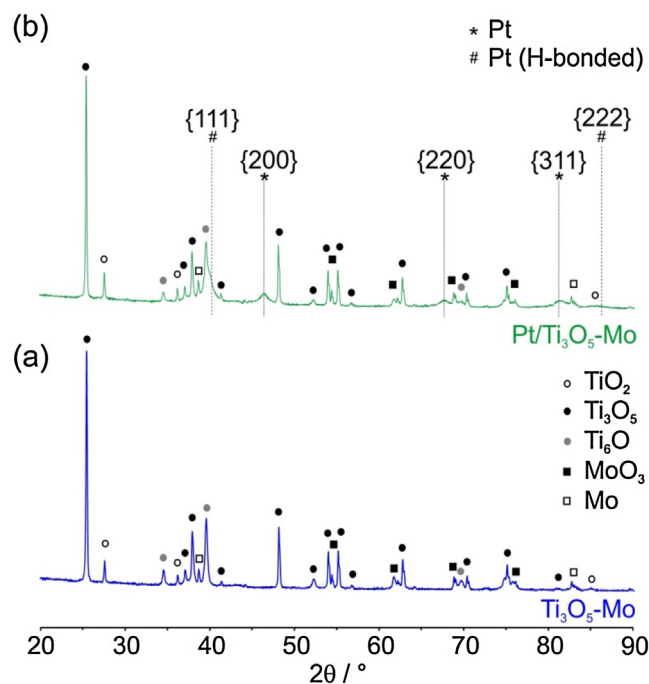


Fig. 1. XRD diffractograms of the  $\text{Ti}_3\text{O}_5$ -Mo support (a), and of the Pt/ $\text{Ti}_3\text{O}_5$ -Mo catalyst (b).

for at least 30 min before the test and was flushed over the cell solution during the measurement. An electrochemical impedance spectroscopy (EIS) measurement was taken at OCV, with a wave amplitude of 10 mV and frequencies in the range of 10 kHz–100 mHz, for the evaluation of the high-frequency resistance (R) of the materials developed.

The stability of the Pt/ $\text{Ti}_3\text{O}_5$ -Mo catalyst and of the  $\text{Ti}_3\text{O}_5$ -Mo support were addressed through APCT by performing 5000 cycles varying the potential in the range of 0–1.2 V vs RHE at a scan rate of 50  $\text{mV s}^{-1}$ , in an  $\text{N}_2$ -saturated 0.5 M  $\text{H}_2\text{SO}_4$  solution [37–39]. According to the DOE protocols [40], this potential range assures the accelerated corrosion of the support as well as the sintering of Pt nanoparticles. For comparison purposes, the stability of the commercial Pt/C was tested in the same conditions, as well, up to 2500 potential cycles. UV–vis measurements were performed on aqueous electrolyte before and after APCT to verify the stability of the  $\text{Ti}_3\text{O}_5$ -Mo, by assessing the absence of Mo and Ti into the solution.

## 3. Results and discussion

### 3.1. Physical-chemical characterization of the $\text{Ti}_3\text{O}_5$ -Mo support and the Pt/ $\text{Ti}_3\text{O}_5$ -Mo catalyst

The crystallographic structure of the materials synthesized is shown in Fig. 1. Fig. 1(a) shows the peaks orientation referring to  $\text{Ti}_3\text{O}_5$  which was synthesized via Mo doping of anatase  $\text{TiO}_2$  at high temperature. In fact, the reduction of  $\text{TiO}_2$  to  $\text{Ti}_3\text{O}_5$  is favored at high temperature, higher than 1200 °C. [21]. The presence of Mo favors the formation of the suboxides in a reducing environment at much lower temperature, 850 °C, as in our case. The corresponding diffractogram displays the Ti in a reduced form, mainly as trititanium pentoxide  $\text{Ti}_3\text{O}_5$  phase (ICDD card no. 01-072-2101) with *Cmcm* orthorhombic structure (main characteristic reflection at  $2\theta = 25.5^\circ$ , {110}). Titanium suboxide phase  $\text{Ti}_6\text{O}$  (ICDD card no. 01-072-1471) is also present, together with few  $\text{TiO}_2$  rutile phase (ICDD card no. 01-088-1173). Thus, our support is a mix of  $\text{Ti}_3\text{O}_5$ ,  $\text{Ti}_6\text{O}$ , and  $\text{TiO}_2$ , with  $\text{Ti}_3\text{O}_5$  being the prevailing Ti sub-

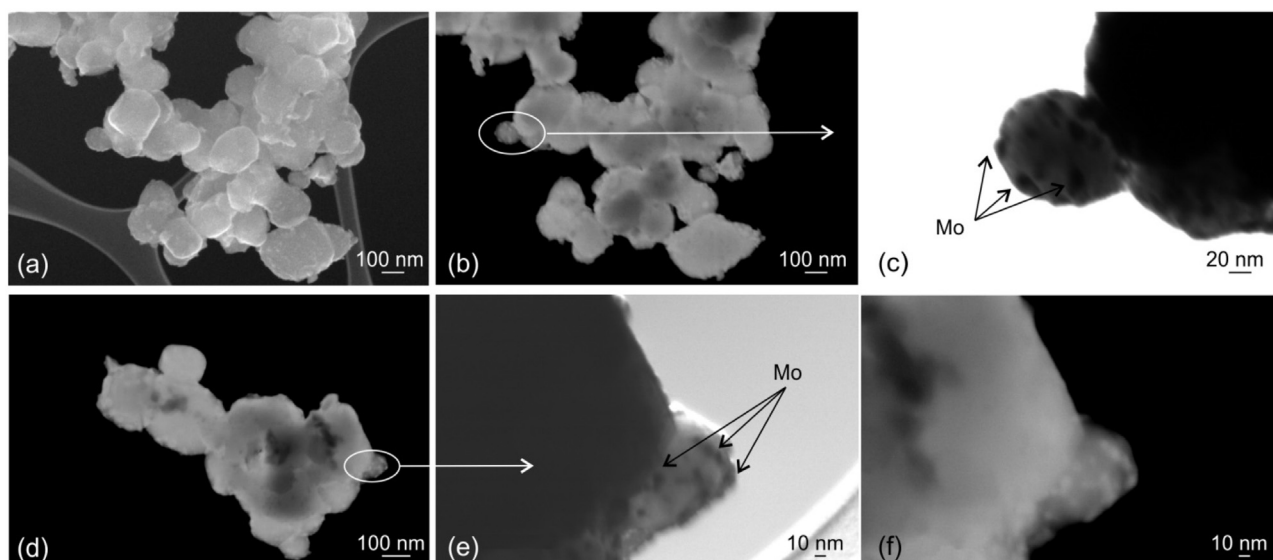


Fig. 2. FESEM-STEM images of two different areas (a/b/c and d/e/f) of the  $\text{Ti}_3\text{O}_5$ -Mo support, at different magnifications to enlighten Mo nanoparticles.

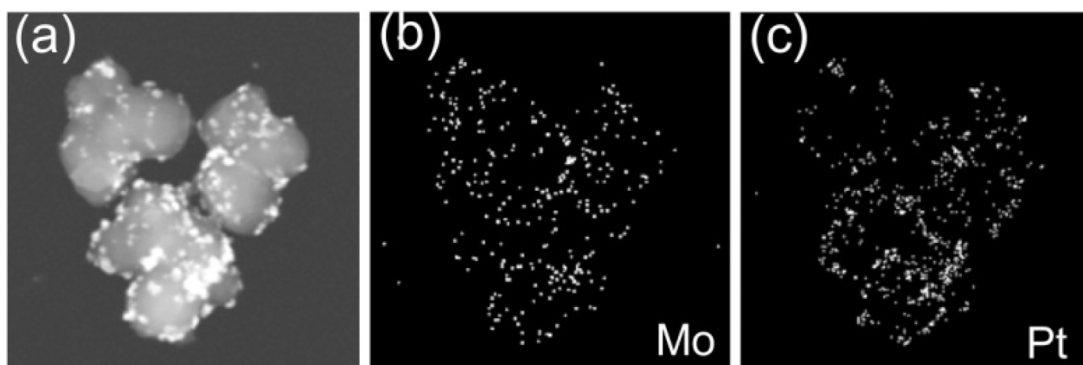


Fig. 3. Back-scattered FESEM image of the  $\text{Pt}/\text{Ti}_3\text{O}_5$ -Mo catalyst (a) with EDX measurements of the Mo (b) and Pt (c) distribution.

oxide phase. Mo is present either as metallic Mo (ICDD card no. 01-088-2331) and  $\text{MoO}_3$  (ICDD card 00-021-0569). According to the literature,  $\text{Ti}_3\text{O}_5$  is a polymorphic compound that can crystallize in several crystallographic phases ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ ) [41]. The orthorhombic structure of the trititanium pentoxide was expected, since, after exposition at a temperature higher than  $250^\circ\text{C}$ , the  $\text{Ti}_3\text{O}_5$  turns into the orthorhombic phase (space group  $\text{Cmcm}$ ), and based on semiconductor-metal transition theory, the compound should exhibit metallic behavior [19,22,23,41,42].

Fig. 1(b) shows the peaks of the  $\text{Pt}/\text{Ti}_3\text{O}_5$ -Mo catalyst, with the corresponding reflections of metallic platinum with face-centered cubic structure. Reflections of Pt are present as pure Pt (ICDD card no. 01-087-0640), with typical reflections at  $2\theta = 46.5^\circ$  {200},  $67.9^\circ$  {220}, and  $81.6^\circ$  {311}, and as Pt H-bonded (ICDD card no. 01-087-0636), with typical reflections at  $2\theta = 40.0^\circ$  {200} and  $85.8^\circ$  {222}. The Pt-H bonded, or [H]-loaded Pt [43] is the synonym for hydrogenated Pt [44,45]. In fact, heating the catalyst at temperatures higher than  $50^\circ\text{C}$  in a reducing atmosphere (in our case:  $450^\circ\text{C}$  in  $\text{H}_2:\text{N}_2$ ) implies the hydrogenation Pt. Under low saturation a  $\text{H}_2$  coordination leads to H–H bond breaking and formation of H–Pt–H hydrides, which agrees with one of the possible reaction pathways of  $\text{H}_2$  side-on cleavage on Pt [46,47]. However upon high saturation,  $\text{H}_2$  molecules symmetrically bind to Pt clusters and remain dimerized [48].

The Pt crystallites size over  $\text{Ti}_3\text{O}_5$ -Mo was calculated as average value from the width of the {200}, {220}, and {311} peaks using

the Scherrer-Debye equation [49,50], resulting in a mean crystallite size of Pt equal to 14 nm. The same calculation on the {111} and {222} peaks of the H-loaded Pt provided a mean crystallite size of Pt equal to 5 nm. The two average values obtained are in fairly good agreement with TEM analysis shown in Fig. 2(d)–(f).

Fig. 2 shows FESEM-STEM images of the  $\text{Ti}_3\text{O}_5$ -Mo support in different areas. The STEM modality allows appreciating the fine distribution of Mo in very small metallic particles. Mo particles cover the entire surface of the support, in a homogeneous way. Fig. 3 shows FESEM-EDX images of the  $\text{Pt}/\text{Ti}_3\text{O}_5$ -Mo, confirming the homogeneous distribution of Pt and Mo nanoparticles over the surface of the support. Fig. 4 shows TEM images at different magnifications of  $\text{Ti}_3\text{O}_5$ -Mo (a, b, and c) and  $\text{Pt}/\text{Ti}_3\text{O}_5$ -Mo (d, e, and f). The  $\text{Ti}_3\text{O}_5$ -Mo support has a well-dispersed series of Mo nanoparticles on the surface of the  $\text{Ti}_3\text{O}_5$ . Mo nanoparticles are in the range of 10–15 nm, confirming the results from FESEM-STEM analysis. Also the  $\text{Pt}/\text{Ti}_3\text{O}_5$ -Mo catalyst has good dispersion and small particle size of Pt, in agreement with XRD and FESEM-EDX analysis.

The XPS high-resolution spectra of the  $\text{Pt}/\text{Ti}_3\text{O}_5$ -Mo catalyst confirm the presence of  $\text{Ti}_3\text{O}_5$  on the surface of the support (Fig. 5). The center of  $\text{Ti}^{3+}$  peak, shown in Fig. 5(a) was located at a binding energy of 457.3 eV, attesting to the presence of  $\text{Ti}_3\text{O}_5$ . The centers of the  $\text{Ti}^{4+}$  with 2  $p_{3/2}$  and 2  $p_{1/2}$  doublet peaks correspond to the binding energies of 459.1 and 464.7 eV, respectively, characteristic of the presence of  $\text{TiO}_2$  phase [51–53]. The Mo high-resolution spectrum in Fig. 5(b) shows the  $\text{Mo}^{6+}$  as the dominant state with



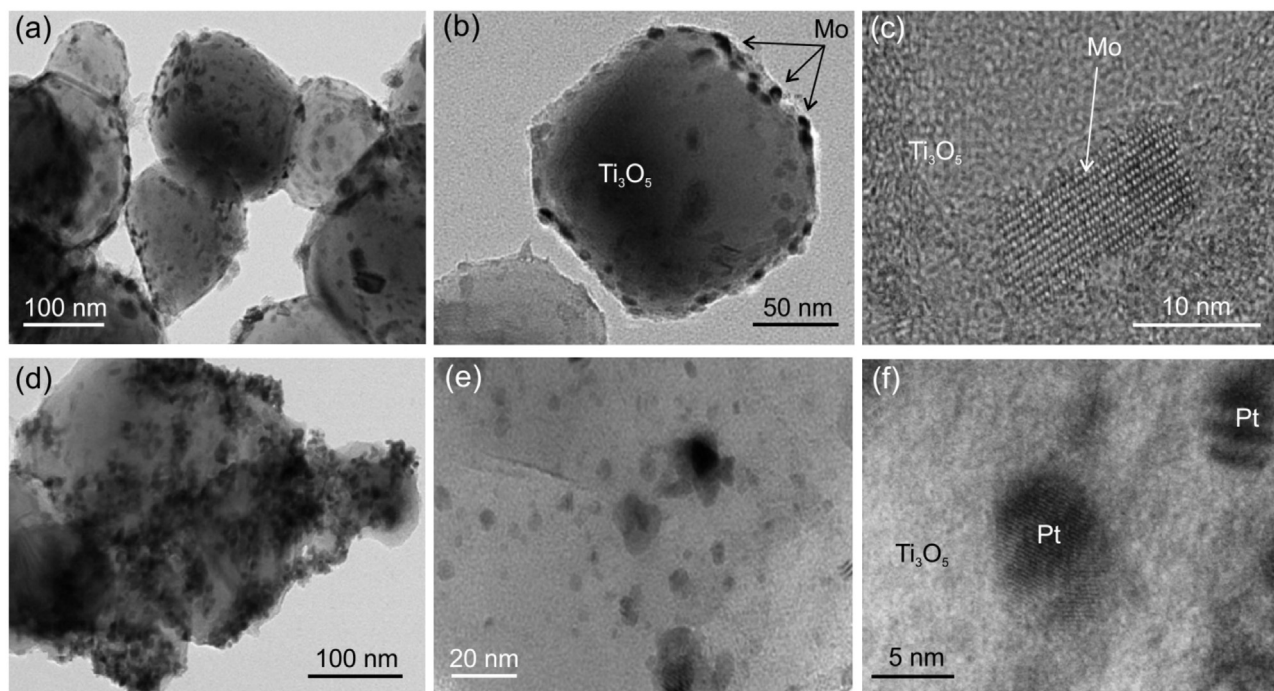


Fig. 4. TEM images of the  $\text{Ti}_3\text{O}_5$ -Mo support (a, b, and c) and of the Pt/ $\text{Ti}_3\text{O}_5$ -Mo catalyst (d, e, and f).

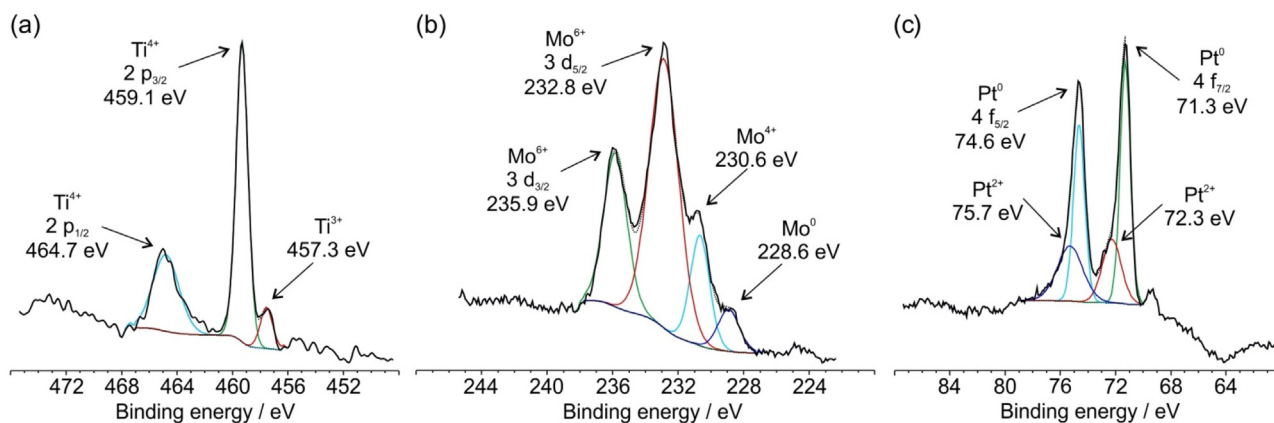
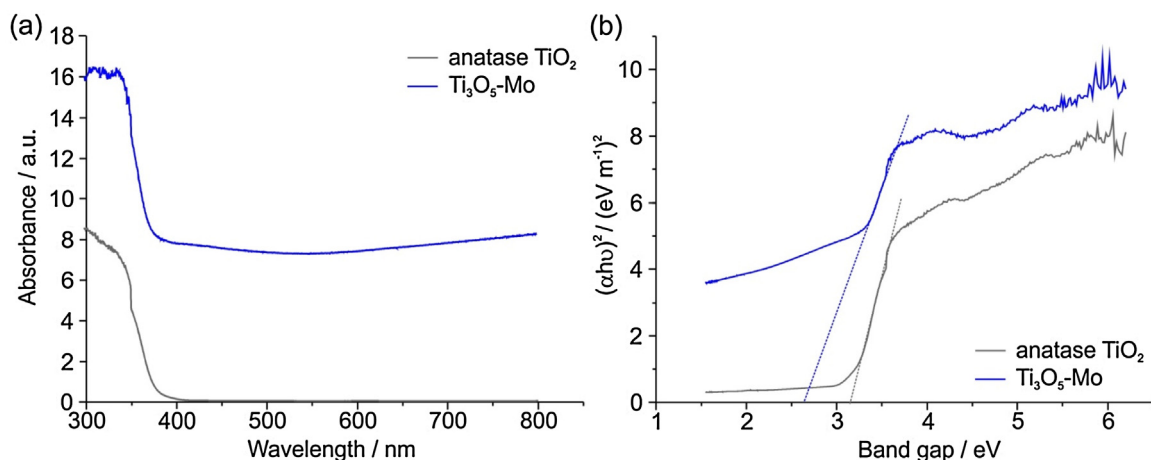


Fig. 5. XPS high-resolution spectra of the Pt/ $\text{Ti}_3\text{O}_5$ -Mo catalyst: Ti (a), Mo (b), and Pt (c).

$3 d_{5/2}$  and  $3 d_{3/2}$  doublet peaks at binding energies of 232.8 eV and 235.9 eV respectively: the peak difference of 3.1 eV is due to the spin-orbit coupling. The Mo metallic and  $\text{Mo}^{4+}$  have lower relative intensity at 228.6 eV and 230.6 eV, respectively [54,55]. The Pt high-resolution spectrum shown in Fig. 5(c) demonstrates spin-orbit splitting doublet peaks in the 4 f region referring to  $4 f_{7/2}$  and  $4 f_{5/2}$ , where the deconvolution of the Pt spectrum reveals two pairs of doublet peaks at each region. The high intense doublet peaks at the binding energies of 71.3 eV and 74.6 eV, respectively, are attributed to metallic Pt. The low-intensity doublet peaks at binding energies of 72.3 eV and 75.7 eV, respectively, appear at 1.2 eV higher in binding energy than that of  $\text{Pt}^0$ , assigned to  $\text{Pt}^{2+}$  species due to surface oxide/hydroxide [55,56]. Besides, the curve fitting of Pt  $4 f_{7/2}$  reveals 0.3 eV positive shift towards higher binding energy compared to the  $4 f_{7/2}$  value of pure Pt, which can be attributed to the positive charge on the dispersed Pt particles interacting with the oxide support [55,57].

The loading of the Pt over the  $\text{Ti}_3\text{O}_5$ -Mo was equal to 15 wt.%, verified by ICP-MS analysis.

Finally, the optical band gap of the starting  $\text{TiO}_2$  and the  $\text{Ti}_3\text{O}_5$ -Mo support was estimated based on the absorption spectra of the diffuse reflectance of the two materials. The reflectance data were converted into the absorption coefficient values according to the Kubelka-Munk equation, as shown in Fig. 6(a) [58,59]. The  $\text{Ti}_3\text{O}_5$ -Mo support has better light spectra absorbance than the starting  $\text{TiO}_2$ . The band gap of the two materials was estimated by applying the Tauc relation, plotting the transformed Kubelka-Munk function as a function of the energy of the excitation source for an indirect semiconductor, Fig. 6(b) [60–63]. The band gap of the  $\text{Ti}_3\text{O}_5$ -Mo support, 2.6 eV, is lower compared to that of  $\text{TiO}_2$ , 3.2 eV. The reference literature value for bulk anatase  $\text{TiO}_2$  is 3.23 eV at 384 nm [61,64], indicating the better conductive properties of the support. Of course, this value is still far from the band gap value of pure  $\text{Ti}_3\text{O}_5$  in the orthorhombic state, ranging from 0.07 to 0.15 eV [19,23,65] with a behavior equivalent to a metal conductor. In fact, in this case according to XRD and XPS analyses, the  $\text{Ti}_3\text{O}_5$ -Mo support contains a mixture of  $\text{Ti}_3\text{O}_5$ ,  $\text{Ti}_6\text{O}$ , and  $\text{TiO}_2$ , with the presence of the  $\text{Ti}^{3+}$  defects and/or oxygen vacancies. In fact, according to the literature

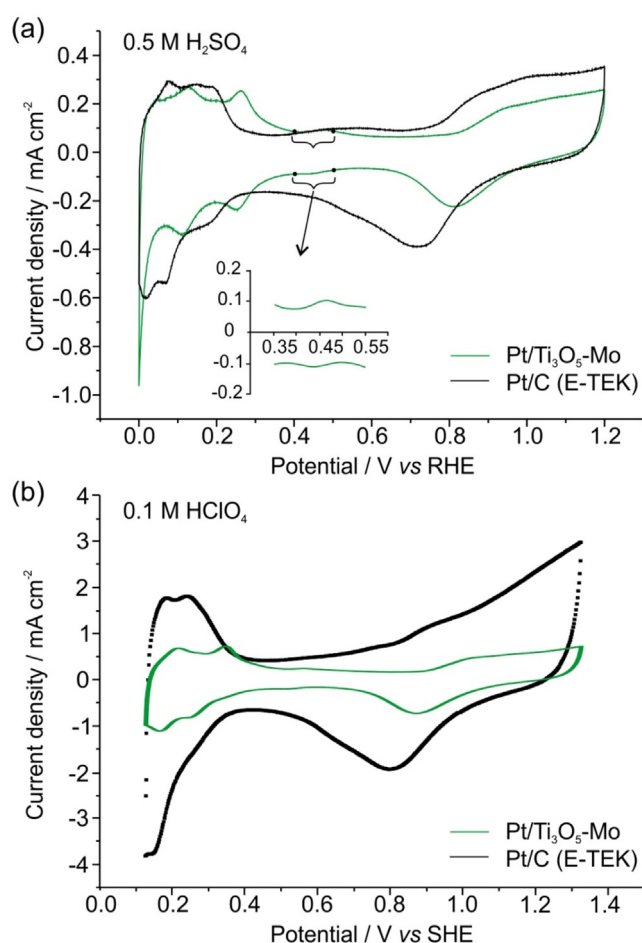


**Fig. 6.** (a) Diffuse reflectance UV-vis spectra according to the Kubelka-Munk equation and (b) transformed Kubelka-Munk function vs. energy of the excitation source (Tauc plot for the indirect allowed transition) of the starting anatase TiO<sub>2</sub> and Ti<sub>3</sub>O<sub>5</sub>-Mo support.

[17–20], Ti<sup>3+</sup> defects and oxygen vacancies are responsible for the *d*–*d* transition. The presence of Ti<sup>3+</sup> species is essential to provide proper electronic conductivity [66]. Definitely, the dark gray color of the Ti<sub>3</sub>O<sub>5</sub>-Mo support, and the black color of the Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo catalyst is an indirect confirmation of the presence of Ti<sup>3+</sup> as well [19]. Last but not least, the molybdenum has a synergetic effect, enhancing the catalytic and photocatalytic properties of the starting materials [25,67]. In fact, doping with some transition metals such as Mo<sup>6+</sup>, W<sup>6+</sup>, and Fe<sup>3+</sup> plays a favorable effect and the energy gap of TiO<sub>2</sub> can be efficiently narrowed [68,69].

### 3.2. Electrochemical characterization of the Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo catalyst

Fig. 7 shows the CVs for Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo and commercial Pt/C catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.1 M HClO<sub>4</sub> measured at 25 °C. The Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo catalyst shows well-known hydrogen ad/desorption characteristics in both electrolytes. Three anodic peaks and three cathodic peaks with reversibility in hydrogen region were assigned to polycrystalline Pt particles over the surface of the support. For both catalysts the polarisation curves exhibit three characteristic regions: the hydrogen ad/desorption peak at low potential range, the double layer capacitance region, and the Pt oxide formation region at high potential, due to the adsorption of oxide/hydroxide on Pt surface. On the other hand, a well-defined cathodic peak at 0.83 and 0.72 V for Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo and Pt/C in sulfuric acid, and 0.86 and 0.80 V for Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo and Pt/C in perchloric acid, respectively, can be attributed to desorption of oxide/hydroxide layer from the Pt surface. The values of the charge transfer resistance of the supports employed, measured via EIS at OCV in the presence of sulfuric acid as electrolyte, were accounted as 6.2 Ω for the Ti<sub>3</sub>O<sub>5</sub>-Mo (5.8 Ω without Nafion® in the ink), 7.5 Ω for the TiO<sub>2</sub>-anatase, and 7.9 Ω for the carbon black (E-TEK). The ESCA of the catalysts, which is determined by the magnitude of the corresponding charge from the hydrogen electro-oxidation peaks (by applying a conversion factor of 210 μC cm<sup>-2</sup>) after subtraction of the double layer capacitance, are listed in Table 1, showing a higher value for the Pt/C in sulfuric acid compared to Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo catalyst. Interestingly, the ECSA values in perchloric acid are higher than that in sulfuric acid. The higher ECSA values in perchloric acid are mainly due to the non-adsorbing or weakly adsorbing properties of HClO<sub>4</sub> as electrolyte [70–73]. The lower ECSA value of Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo compared to Pt/C can be attributed to the low specific surface area of the Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo, around 10 m<sup>2</sup> g<sup>-1</sup>, because of the prolonged heat treatment under H<sub>2</sub>/N<sub>2</sub> atmosphere to form oxygen vacancies. Similar values were



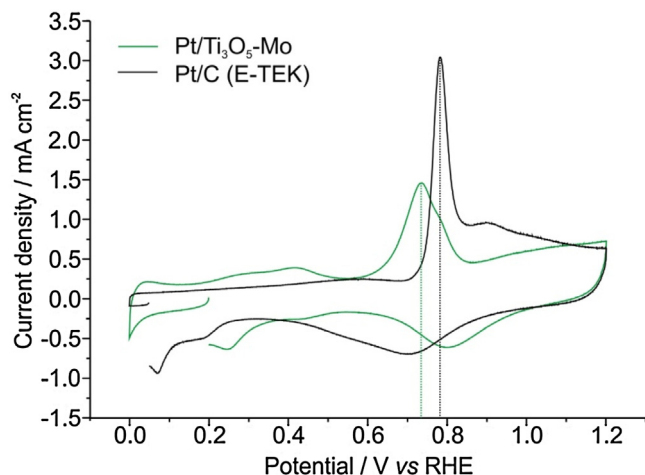
**Fig. 7.** CV of the Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo and Pt/C recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub> (a), and in 0.1 M HClO<sub>4</sub> (b). For both cases: scan rate of 10 mV s<sup>-1</sup> at 25 °C (catalyst loading: 15 μg<sub>Pt</sub> cm<sup>-2</sup>, 0.1 ITC mass ratio).

obtained for Pt/TiOx-C catalysts heat treated at 1000 °C in reducing atmosphere [36].

Moreover, the CV of Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo in sulfuric acid shows redox peaks between 0.38 and 0.52 V vs RHE. These peaks are attributed to the faradaic process of intercalation/de-intercalation of H atoms into MoO<sub>y</sub> lattice, with formation hydrogen molybdenum bronzes. This is due to the well-known fact which MoO<sub>y</sub> in the presence of

**Table 1**Electrochemical characterization of Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo and Pt/C (E-TEK) catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.1 M HClO<sub>4</sub> as electrolytes. Data calculated from Figs. 7–9.

	Pt [mg cm <sup>-2</sup> ]	Q <sub>H</sub> [mC cm <sup>-2</sup> ]	ECSA <sub>H<sub>2</sub></sub> @ H <sub>2</sub> SO <sub>4</sub> [m <sup>2</sup> g <sup>-1</sup> ]	ECSA <sub>H<sub>2</sub></sub> @ HClO <sub>4</sub> [m <sup>2</sup> g <sup>-1</sup> ]	ECSA <sub>CO</sub> @ H <sub>2</sub> SO <sub>4</sub> [m <sup>2</sup> g <sup>-1</sup> ]	I @ 0.9 V, H <sub>2</sub> SO <sub>4</sub> [mA cm <sup>-2</sup> ]	Specific activity @ 0.9 V, H <sub>2</sub> SO <sub>4</sub> [mA cm <sub>Pt</sub> <sup>-2</sup> ]
Pt/Ti <sub>3</sub> O <sub>5</sub> -Mo	0.015	0.540	22.3	33.1	66.3	1.1	2.1
Pt/C (E-TEK)	0.020	0.616	39.5	44.2	70.4	0.7	0.3

**Fig. 8.** CV of CO oxidation on Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo and Pt/C E-TEK recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub>, scan rate of 20 mV s<sup>-1</sup> at 25 °C (catalyst loading: 15 μg<sub>Pt</sub> cm<sup>-2</sup>, 0.1 ITC mass ratio).

noble metals absorb the hydrogen at room temperature and forms H<sub>x</sub>MoO<sub>y</sub>: xH<sup>+</sup> + xe<sup>-</sup> + MoO<sub>y</sub> ↔ H<sub>x</sub>MoO<sub>y</sub> [55,74–76].

The hydrogen evolution reaction (HER) of Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo in sulfuric acid (Fig. 7a) occurs at slightly lower potential range compared to Pt/C. The reasons could lie in the electrical conductivity of the Ti<sub>3</sub>O<sub>5</sub>-Mo support. In fact, according to the band gap measurements (Fig. 6), Ti<sub>3</sub>O<sub>5</sub>-Mo has a higher band gap valued compared to the theoretical value of the Ti<sub>3</sub>O<sub>5</sub>, sign that the support is accompanied by other compounds which affect the electrical conductivity. Indeed, XRD analyses showed that the support is a mix of Ti<sub>3</sub>O<sub>5</sub>, Ti<sub>6</sub>O, and TiO<sub>2</sub>, with Ti<sub>3</sub>O<sub>5</sub> being the prevailing Ti suboxide phase. This fact could explain the shift of the HER. Moreover, the presence of Mo, both in the form of metallic Mo and MoO<sub>3</sub>, could play a role in the shift of the HER, as explained in the literature [6,8,37,77,78]. Furthermore, according to Markovic et al. [79] the under-potentially deposited hydrogen, H<sub>upd</sub>, and the weakly adsorbed states as the reactive intermediate, H<sub>ad</sub>, could play a role as well. In fact, the H<sub>upd</sub> is strongly dependent on the crystallographic orientation of the Pt surface [80]. The weakly adsorbed state of H<sub>ad</sub> on Pt single crystals could couple to the strongly adsorbed state of the H<sub>upd</sub>, with a consequent indirect effect of the H<sub>upd</sub> on the kinetics. Thus, H<sub>upd</sub> might play an important role in the kinetics of the HER, and the HOR as well, in aqueous electrolyte solutions.

To investigate the influence of the suboxide support on Pt catalyst in the presence of CO species, a CO stripping test was performed for both catalysts, Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo and Pt/C, in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 25 °C, as shown in Fig. 8. The results of CO stripping over Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo catalyst show the onset potential corresponding to the CO oxidation reaction shift toward the lower potential value, with the peak potential appearing at 0.74 V vs RHE while for Pt/C the peak potential appeared at 0.79 V vs RHE. Apart from the main oxidation peak, there is a minor pre-peak at a lower potential for Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo, as an early onset potential, due to the oxidation of weakly bonded CO. The early onset of CO oxidation as a pre-peak is typical of catalysts alternating Pt-containing layers and layers containing suboxides of a second metal, such as Ti, Ta, W, and Mo [81,82]. The results indicated the Ti<sub>3</sub>O<sub>5</sub>-Mo support, through the oxygen vacancies which

formed in close contact to Pt nanoparticles, could supply a source of hydroxyl intermediates (OH) which extends the active surfaces for oxidation of CO to CO<sub>2</sub> and polishing the Pt active site from CO poisoning species [16,83,84]. Moreover, since the CO species can only be adsorbed on the surface of the Pt atoms (active site), the CO oxidation charge can be converted into the surface area by applying a conversion factor of 420 μC cm<sup>-2</sup>, as used for polycrystalline Pt [85,86]. Consequently, the active Pt surface area of the electrodes are 1.25 cm<sub>Pt</sub><sup>2</sup> and 1.77 cm<sub>Pt</sub><sup>2</sup> for Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo and commercial Pt/C, respectively. These values, converted into m<sup>2</sup> g<sup>-1</sup>, are listed in Table 1 for a comparison with the ECSA values calculated from the hydrogen underpotential deposition.

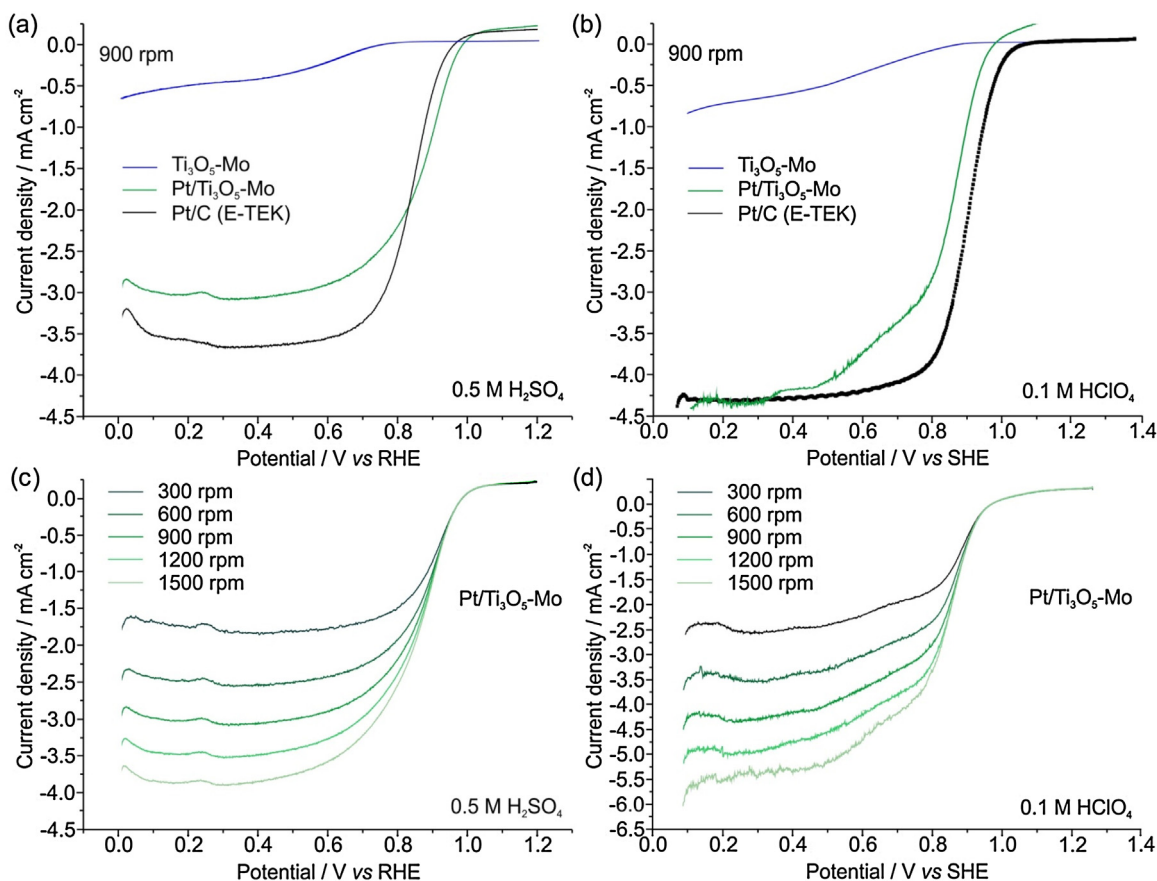
The ORR is a complex multi-step reaction involving the exchange of four electrons to form water, which is the desired reaction pathway [87]. Fig. 9(a) and (b) shows the ORR activities of Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo and Pt/C catalysts in 0.5 M H<sub>2</sub>SO<sub>4</sub> and 0.1 M HClO<sub>4</sub>, respectively, at 25 °C purged by O<sub>2</sub> at 900 rpm. The activity of the sole support, Ti<sub>3</sub>O<sub>5</sub>-Mo, is reported as well for comparison purposes. In sulfuric acid the Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo catalyst exhibits considerable activity toward ORR with a high onset potential of O<sub>2</sub> reduction as well as a half-wave potential, which is achieved at 0.86 V vs RHE (compared to a half-wave potential of 0.84 V vs RHE for the commercial Pt/C). The ORR polarisation curve shows that both catalysts display diffusion control when the potential is less than 0.65 V vs RHE, reaching limiting current densities between 3–3.5 mA cm<sup>-2</sup>. The lower values of the limiting currents at 900 rpm in sulfuric acid for both catalysts could be linked with the adsorbing properties of H<sub>2</sub>SO<sub>4</sub> as electrolyte. In fact, the sulfate, and phosphate, anion adsorption poisons the Pt surface. As a consequence, it is expected that the activity in sulfuric acid decreases dramatically. Interestingly, according to the literature, Pt/Ti-suboxides catalysts are able to counteract the anion adsorption poisoning due to surface modification of Ti-suboxides by sulfate anions, which increase the charge transfer of the support by modifying the electric conductivity [15,52,88–90].

In perchloric acid the Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo catalyst exhibits slightly lower activity toward ORR compared to Pt/C, with a half-wave potential of 0.85 V vs SHE (compared to a half-wave potential of 0.90 V vs SHE for Pt/C). The ORR polarisation curves show that both catalysts display the diffusion control region for potential lower than 0.65 V vs RHE, reaching the expected limiting current densities around 4.3 mA cm<sup>-2</sup> at 900 rpm.

The specific activity of the Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo, and Pt/C in sulfuric acid was calculated determining the ORR kinetic current *i<sub>k</sub>* considering the mass transport, using the relationship established by the Koutecky–Levich theory, and normalizing with the specific surface area of Pt. The activity of electrocatalysts was calculated from the experimental data using the mass-transport correction for rotating disk electrodes. The calculated values at 0.9 V vs RHE, listed in Table 1, are 2.1 mA cm<sub>Pt</sub><sup>-2</sup> for Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo and 0.3 mA cm<sub>Pt</sub><sup>-2</sup> for Pt/C, respectively.

For ORR mechanism understanding, the LSV were collected at different rotational speeds, both in sulfuric and perchloric acid, as shown in Fig. 9(c) and (d), respectively. Diffusion-limited current densities collected at different rotation rates in the potential range from 0.2 to 0.8 V vs RHE were used to determine the number of electrons transferred associated with ORR, which was calculated





**Fig. 9.** ORR for  $\text{Ti}_3\text{O}_5$ -Mo,  $\text{Pt}/\text{Ti}_3\text{O}_5$ -Mo, and  $\text{Pt}/\text{C}$  (E-TEK) recorded at a scan rate of  $5 \text{ mV s}^{-1}$  at  $25^\circ\text{C}$  and 900 rpm (Pt loading:  $15 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ , 0.1 ITC mass ratio) in  $0.5 \text{ M H}_2\text{SO}_4$  (a) and  $0.1 \text{ M HClO}_4$  (b). ORR for  $\text{Pt}/\text{Ti}_3\text{O}_5$ -Mo at different rotational speeds in  $0.5 \text{ M H}_2\text{SO}_4$  (c) and  $0.1 \text{ M HClO}_4$  (d).

to be almost 4 (from 3.86 to 4.17) by the Koutecky–Levich equation in sulfuric acid (not shown here), suggesting a complete reaction to water with a very limited hydrogen peroxide production.

Overall, the  $\text{Pt}/\text{Ti}_3\text{O}_5$ -Mo showed promising performance with a mass activity of  $\sim 73 \text{ mA mg}_{\text{Pt}}^{-1}$ , which is almost double of the  $\text{Pt}/\text{C}$  benchmark catalyst, in agreement with literature data [5,85].

### 3.3. Stability of the $\text{Pt}/\text{Ti}_3\text{O}_5$ -Mo catalyst

Besides high electrocatalytic activity, the stability of the catalyst is an important characteristic that was evaluated for the  $\text{Ti}_3\text{O}_5$ -Mo support, the  $\text{Pt}/\text{Ti}_3\text{O}_5$ -Mo catalyst, and the commercial  $\text{Pt}/\text{C}$ , as well (Fig. 10). The stability of the  $\text{Ti}_3\text{O}_5$ -Mo and  $\text{Pt}/\text{Ti}_3\text{O}_5$ -Mo was assessed up to 5000 potential cycling in sulfuric acid. The  $\text{Ti}_3\text{O}_5$ -Mo is perfectly stable in  $0.5 \text{ M H}_2\text{SO}_4$  aqueous electrolyte over the full range of applied potential cycling, Fig. 10(a). The CV curves have nearly rectangular shapes with small reversible redox peaks, typical for pseudo-capacitive materials [29]. The  $\text{Pt}/\text{Ti}_3\text{O}_5$ -Mo, Fig. 10(b), shows limited loss of performance. The double layer region shows constant capacity for all cycles, a sign that the  $\text{Ti}_3\text{O}_5$ -Mo support is a stable and durable support. Instead, Fig. 10(c), the  $\text{Pt}/\text{C}$  shows a huge performance decay just after 2500 cycles, with a noticeable reduction of the hydrogen desorption-adsorption peaks, demonstrating the commercial catalyst as an unstable catalyst for ORR.

Fig. 11 shows the losses of ECSA calculated from Fig. 10, for the two Pt-based catalysts. The  $\text{Pt}/\text{Ti}_3\text{O}_5$ -Mo the ECSA loss was very limited after 5000 APCT cycles, only 11.2%. In fact, according to the literature [13,36,37,91–93], the  $\text{Ti}_3\text{O}_5$  suboxide available on the surface of the catalyst does not contribute during hydrogen ad/desorption regime but has a major influence on the stability of

the catalyst itself. No Ti oxidation was observed during the CVs performance, Fig. 10(a), a sign that  $\text{Ti}_3\text{O}_5$ -Mo remained stable. For the  $\text{Pt}/\text{C}$ , as expected, notwithstanding the higher starting ECSA value, it reduced dramatically because of the corrosion of the carbon support and the consequent Pt particles migration and sintering, reaching an overall ECSA loss of more than 81%.

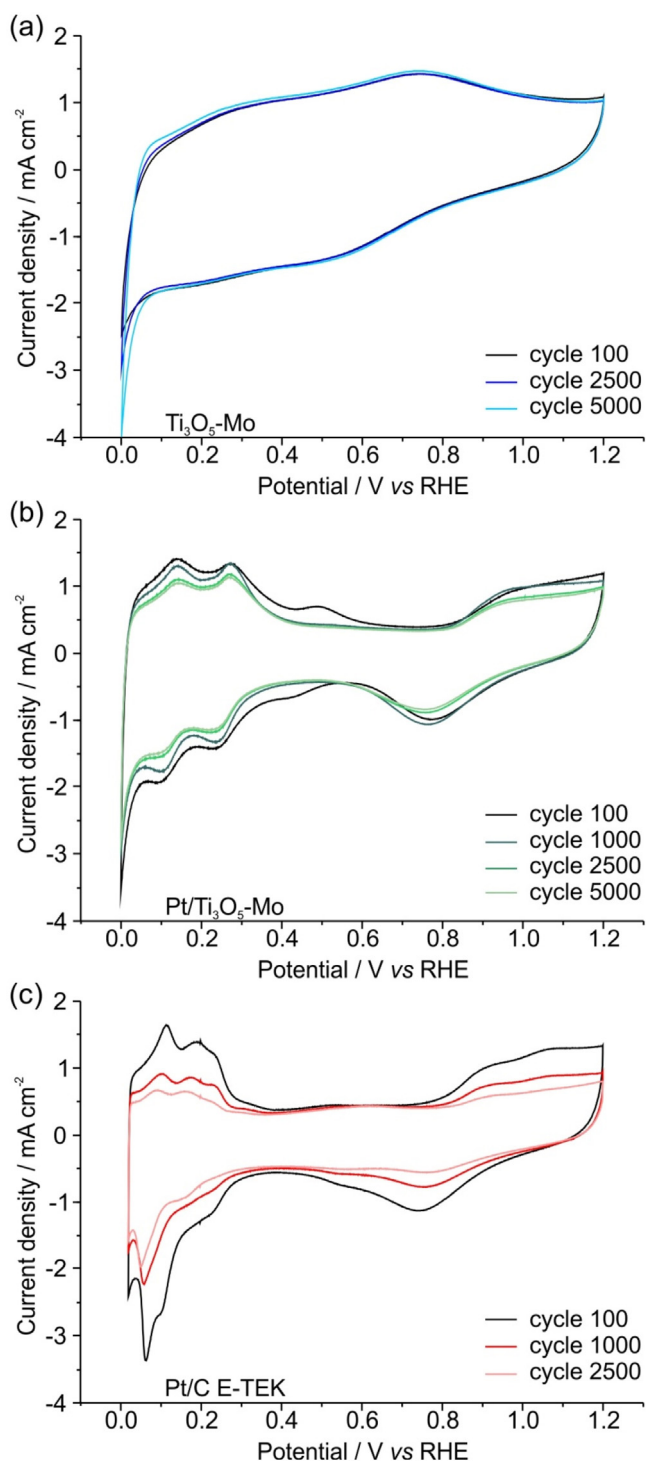
To further assess the stability of both the  $\text{Ti}_3\text{O}_5$ -Mo and the  $\text{Pt}/\text{Ti}_3\text{O}_5$ -Mo, UV–vis measurements were performed on the aqueous electrolytes of the two catalysts before and after APCT measurements, resulting in no variation in each electrolyte solution, Fig. 12, which prove that the  $\text{Ti}_3\text{O}_5$ -Mo is a very stable support in acidic electrolytes.

Finally, to assess the good performance of the  $\text{Pt}/\text{Ti}_3\text{O}_5$ -Mo catalyst, LSV and CO stripping measurements were repeated after the APCT procedure. Results in Fig. 13(a) show that the ORR activity is only slightly affected by the APCT procedure, with a shift of 0.05 V of the half-wave potential (from 0.86 to 0.81 V vs RHE). At 0.9 V vs RHE, the current density decreased from 1.1 to 0.6  $\text{mA cm}^{-2}$ . From the CO stripping results, Fig. 13(b), the peak potential appearing at 0.74 V vs RHE for the fresh  $\text{Pt}/\text{Ti}_3\text{O}_5$ -Mo shifted to 0.75 V vs RHE. Their minor pre-peak at a lower potential, typical of the presence of Ti-suboxide layers [81,82], shifted as well to slightly higher potential. The calculated mass activity at 0.9 V vs RHE after APCT reached the value of  $40 \text{ mA mg}_{\text{Pt}}^{-1}$ . These results clearly demonstrate that the  $\text{Pt}/\text{Ti}_3\text{O}_5$ -Mo is a highly active and stable catalyst toward ORR.

## 4. Conclusions

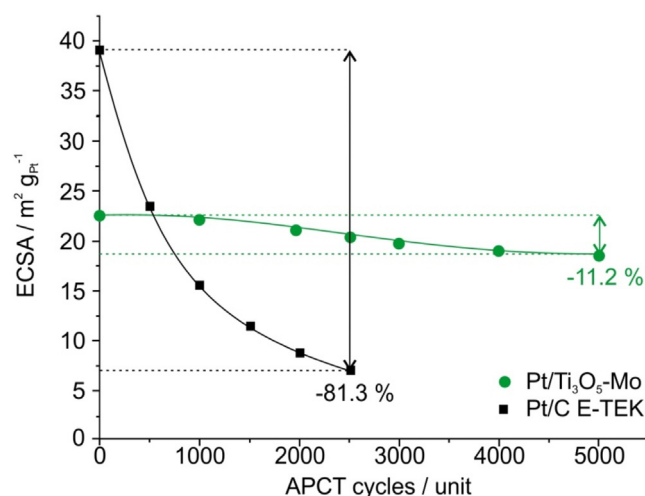
A  $\text{Pt}/\text{Ti}_3\text{O}_5$ -Mo catalyst was synthesized by modifying commercial anatase  $\text{TiO}_2$  with Mo into  $\text{Ti}_3\text{O}_5$ -Mo suboxide, and further



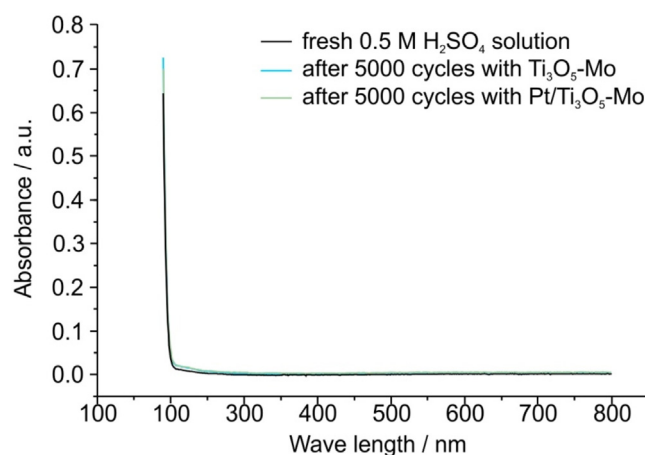


**Fig. 10.** APCT tests performed on (a) Ti<sub>3</sub>O<sub>5</sub>-Mo, (b) Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo, and (c) Pt/C E-TEK, recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 25 °C, in the range 0–1.2 V vs RHE at a scan rate of 50 mV s<sup>-1</sup>.

deposition of 15 wt.% Pt. The Pt-based carbon-free catalyst was fully characterized and tested for the oxygen reduction reaction, using both sulfuric and perchloric acid as electrolyte. Its performance was compared to that of commercial Pt/C from E-TEK, demonstrating a good performance of 73.3 mA mg<sup>-1</sup>, with a current density of 1.1 mA cm<sup>-2</sup> at 0.9 V vs RHE compared to the 0.7 mA cm<sup>-2</sup> at 0.9 V vs RHE of the commercial one. A deep accelerated potential cycling between 0 and 1.2 V vs RHE up to 5000 cycles demonstrated



**Fig. 11.** ECSA trends according to APCT for the Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo and Pt/C E-TEK catalysts. Data calculated from Fig. 10(b) and (c).

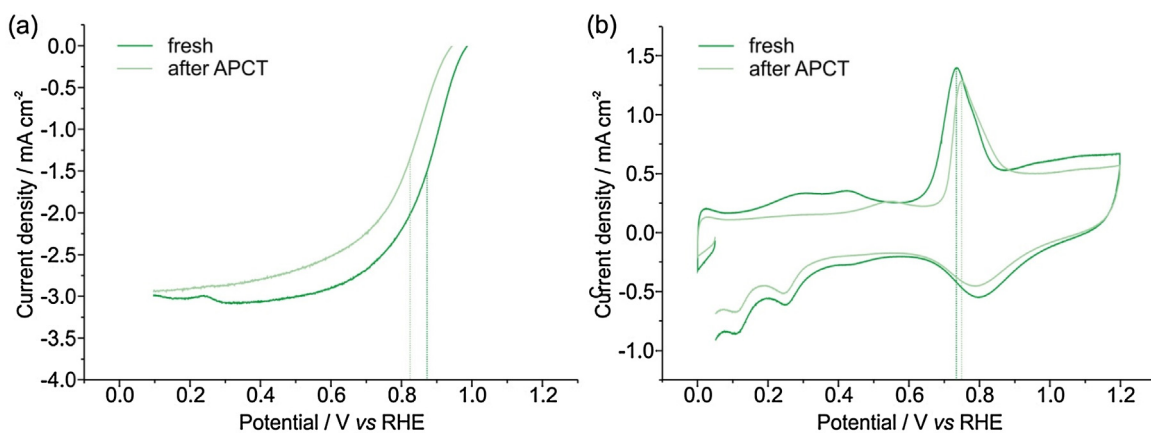


**Fig. 12.** UV absorption spectra of 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous electrolyte before and after APCT tests (up to 5000 cycles) for Ti<sub>3</sub>O<sub>5</sub>-Mo and Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo.

the remarkable stability of the Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo catalyst, whose ECSA loss was accounted for only 11%, compared to the more than 81% loss of the commercial Pt/C reference, notwithstanding a starting ECSA value almost the double of the Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo catalyst. The stable performance was attributed to the positive effect of the doped Ti<sub>3</sub>O<sub>5</sub>-Mo suboxide in stabilizing the Pt probably because of a change in the *d*-band length of the Ti<sub>3</sub>O<sub>5</sub>-Mo support. Thus, the Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo can be considered as an innovative stable carbon-free alternative catalyst for ORR for PEMFC applications.

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**Fig. 13.** (a) comparison of ORR for Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo before and after APCT, recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub>, scan rate of 5 mV s<sup>-1</sup> at 25 °C and 900 rpm. (b) comparison of CV of CO oxidation on Pt/Ti<sub>3</sub>O<sub>5</sub>-Mo before and after APCT, recorded in 0.5 M H<sub>2</sub>SO<sub>4</sub>, scan rate of 20 mV s<sup>-1</sup> at 25 °C (for both cases, catalyst loading: 15 μgPt cm<sup>-2</sup>, 0.1 ITC mass ratio).

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